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Preliminary communication

HYDRIDIC CHARACTER OF EARLY TRANSITION METAL HYDRIDE COMPLEXES

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Summary

The cendency of transition metal hydride complexes to behave as true hydrides, as measured by ability to reduce ketones, appears to depend strongly on the position of the metal in the Periodic Table; the strongest such behavior is exhibited by complexes of metals furthest to the left in the transition series.

Complexes with transition metal-to-hydrogen bonds are called hydrides, and are formulated as being polarized $M^{+}-H^{-}$ for the purpose of assigning a formal oxidation state to the metal; however, little attention has been paid to the question of when, if ever, they manifest such polarization in their reactivity. While acidic character of transition metal hydrides is common (1), reactivity typical of hydridic behavior, such as facile reaction with water or alcohols to give hydrogen, or reduction of carbonyl compounds,** has been reported for only a few compounds (2,3). It is noteworthy that the latter are all of group IVa metals,

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**This does not include catalytic hydrogenation of aldehydes and ketones, which is more common; however, it is not clear that such reactions are true indications of hydridic character in the metal hydride.

TABLE

Reactions of Metal Hydrides with Ketones

Complex	With CH_3COCH_3[a]	With CF_3COCH_3[a]	τM-H	IP (eV)[b]
Cp_2ZrH_2	inst.[c]	d	2.5[e]	
$(CpTiH)_2C_{10}H_8$	inst.	d		
Cp_2NbH_3	12 hours	inst.	12.7,13.7	
Cp_2TaH_3	d	inst.	11.6,13.0	8.1
$Cp_2NbH(CO)$	2 days	inst.	16.5	
Cp_2MoH_2	nr (78°)	1 day	16.1	8.9
$CpMo(CO)_3H$	nr (78°)	nr (78°)	15.6	
Cp_2ReH	nr (78°)	nr (78°)	23.3	(8.8-10.2)[f]

[a] Approximate time for complete disappearance of hydride complex, at room temperature unless otherwise indicated. inst. = instantaneous; nr = no reaction detected. [b] Lowest energy photoelectron band assigned to M-H bonding orbital (6). [c] Ref. 5. [d] Reaction not examined. [e] Shift reported for $(C_5Me_5)_2ZrH_2$ (7). [f] M-H band overlaps with others in this region, so exact value uncertain (6).

Ti and Zr, suggesting that position in the Periodic Table might be a key factor. In connection with our hypothesis that hydridic character may be related to CO-reducing ability (4), we are investigating the occurrence of such behavior, and here report preliminary results.

Using the ability to reduce ketones as a test of hydridic character, we have found that cyclopentadienylmetal hydrides of groups IVa-VIa exhibit such character, with the degree (as determined by reaction rate) decreasing on moving from left to right across the transition series. Results are summarized in the Table: hydrides of group IVa react rapidly with acetone; those of Va react slowly with acetone but rapidly with the more electrophilic ketone 1,1,1-trifluoroacetone; and so on. In all cases where reaction occurred, the corresponding alcohols were obtained in high yield* following hydrolysis and distillation. The probably initial products, metal alkoxides, could not be isolated (with the exception of $Cp_2Zr(OCH(CH_3)_2)$ (5) and appear to be generally unstable, although in some cases they could be observed as intermediates by nmr. Characterization of the various metal-containing products is in progress.

Hydridic character appears to depend to some degree on the ligands present as well as the metal; in particular, it seems to be reduced by CO in the complex, as would be expected: electron-withdrawing ligands <u>enhance</u> acidic character (1). It may be noted that there is some correlation between hydridic character and decreasing ionization potential of the M-H bonding electrons;

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*Reactions were carried out in benzene with 2-3 fold excess of ketone, and rates monitored by disappearance of nmr peaks of complex; alcohols were determined by nmr and vpc. Within experimental error, 1 mole of alcohol per hydride ligand was obtained for all complexes except Cp_2MH_3 (M = Nb, Ta) for which the yield was <u>ca.</u> 2 moles of alcohol per metal atom.

this is reasonable if the latter is a measure of negative charge density on H, although the data available are limited (6). Only a very rough correlation to the nmr shift of the hydrides is seen. (For the complexes Cp_2MH_x only, there is a trend of increasing hydridic behavior with downfield shift.) While the physica interpretation of these results must remain uncertain, the empirical relationship between hydridic character and position in the Periodic Table appears to be definite.

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